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(54) OXIDATION INHIBITED PHOSPHATE BASED HYDRAULIC FLUIDS

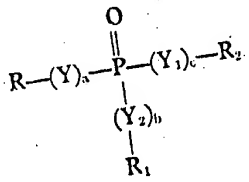
(71) We, STAUFFER CHEMICAL COMPANY, a corporation organised under the laws of the State of Delaware, United States of America, of Dobbs Ferry, New York 10522, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to oxidation inhibited phosphate-based fluids.

We have found that phosphate ester and amide based fluids are unexpectedly improved in oxidative stability by incorporating therein synergistic combinations of certain hydrogen phosphates and a certain hindered phenols.

According to the invention there is provided a fluid comprising:

(a) a phosphate base stock having the formula:



wherein Y is oxygen, sulfur or

Y_1 is oxygen sulfur or

Y_2 is oxygen, sulfur or

R, R_1, R_2, R_3, R_4 and R_5 are each an alkyl, aryl, substituted aryl or substituted alkyl; and a, b and c are each 0 or 1 and the sum a+b+c is from 1 to 3; and

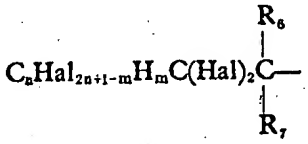
(b) an oxidative stabilising amount of an antioxidant combination of a hydrogen phosphate ester (as hereinafter defined) and a hindered phenol (as hereinafter defined).

In the phosphate base stock of the above formula, typical examples of alkyl radicals are: methyl, ethyl, normal propyl, isopropyl, normal butyl, isobutyl, secondary butyl, tertiary butyl, normal amyl, isoamyl, 2-methylbutyl, 2,2-dimethyl propyl, 1-methyl butyl, diethylmethyl, 1,2-dimethyl propyl, tertiary amyl, normal hexyl, 1-

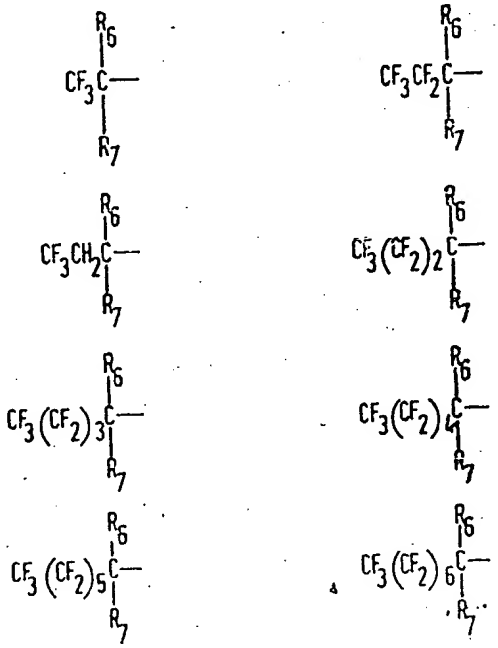
methylamyl, 1-ethyl butyl, 1,2,2-trimethyl propyl, 3,3-dimethyl butyl, 1,1,2-trimethyl propyl, 2-methyl amyl, 1,1-dimethyl butyl, 1-ethyl 2-methyl propyl, 1,3-dimethyl butyl, isohexyl, 3-methylamyl, 1,2-dimethyl butyl, 1-methyl 1-ethyl propyl, 2-ethyl butyl, normal heptyl, 1,1,2,3-tetramethyl propyl, 1,2-dimethyl 1-ethyl propyl, 1,1,2-trimethyl butyl, 1-isopropyl 2-methyl propyl, 1-methyl 2-ethyl butyl, 1,1-diethyl propyl, 2-methyl hexyl, 1,1-dimethyl amyl, 1-isopropyl butyl, 1-ethyl 3-methyl butyl, 1,4-dimethyl amyl, isoheptyl, 1-methyl 1-ethyl butyl, 1-ethyl 2-methyl butyl, 1-methyl hexyl, 1-propyl butyl, normal octyl, 1-methyl heptyl, 1,1-diethyl 2-methyl propyl, 1,1,3,3-tetramethyl butyl, 1,1-diethyl butyl, 1,1-dimethyl hexyl, 1-methyl 1-ethyl amyl, 1-methyl 1-propyl butyl, 2-ethyl hexyl, 6-methyl heptyl (isooctyl), normal nonyl, 1-methyl octyl, 1-ethyl heptyl, 1,1-dimethyl heptyl, 1-ethyl 1-propyl butyl, 1,1-diethyl 3-methyl butyl, diisobutyl methyl, 3,5,5-trimethyl hexyl, 3,5-dimethyl heptyl, normal decyl, 1-propyl heptyl, 1,1-diethyl hexyl, 1,1-dipropyl butyl, 2-isopropyl 5-methyl hexyl and C_{11}—C_{18} alkyl groups. Also included are aralkyl groups, e.g. benzyl, alpha- or beta-phenylethyl, and alpha-alpha dimethyl benzyl groups. Also included are cyclohexyl and cycloheptyl groups.

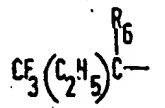
Preferably, R, R_1 and R_2 are each a phenyl, cresyl, xylyl, isopropylphenyl, biphenylyl or α-methylbenzylphenyl group.

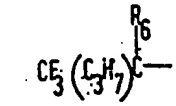
Typical examples of substituted alkyl radicals are the haloalkyl radicals which can be represented by the structure:

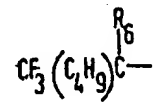


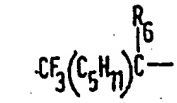
where Hal refers to a halogen, m is less than or equal to 2n+1 and n may have any value from 0 to 18, and R_6 and R_7 can be hydrogen, halogen or alkyl radicals. Preferred radicals are those where Hal is fluoro and include those represented by the following formulae:

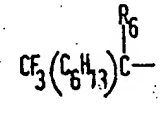


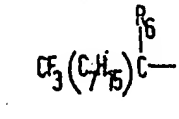


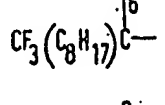


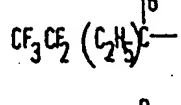


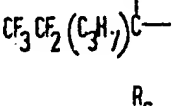


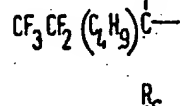


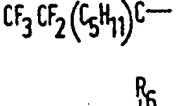


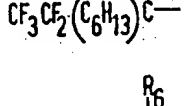


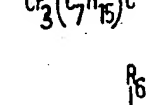


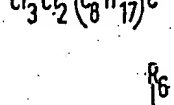


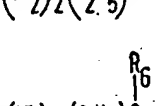


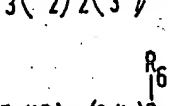


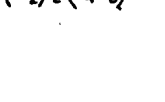


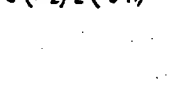


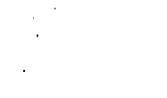












$$CF_3(C_2H_5)\overset{R_6}{\overset{|}{C}}- \qquad CF_3(C_3H_7)\overset{R_6}{\overset{|}{C}}-$$

$$CF_3(C_4H_9)\overset{R_6}{\overset{|}{C}}- \qquad CF_3(C_5H_{11})\overset{R_6}{\overset{|}{C}}-$$

$$CF_3(C_6H_{13})\overset{R_6}{\overset{|}{C}}- \qquad CF_3(C_7H_{15})\overset{R_6}{\overset{|}{C}}-$$

$$CF_3(C_8H_{17})\overset{R_6}{\overset{|}{C}}- \qquad CF_3CF_2(C_2H_5)\overset{R_6}{\overset{|}{C}}-$$

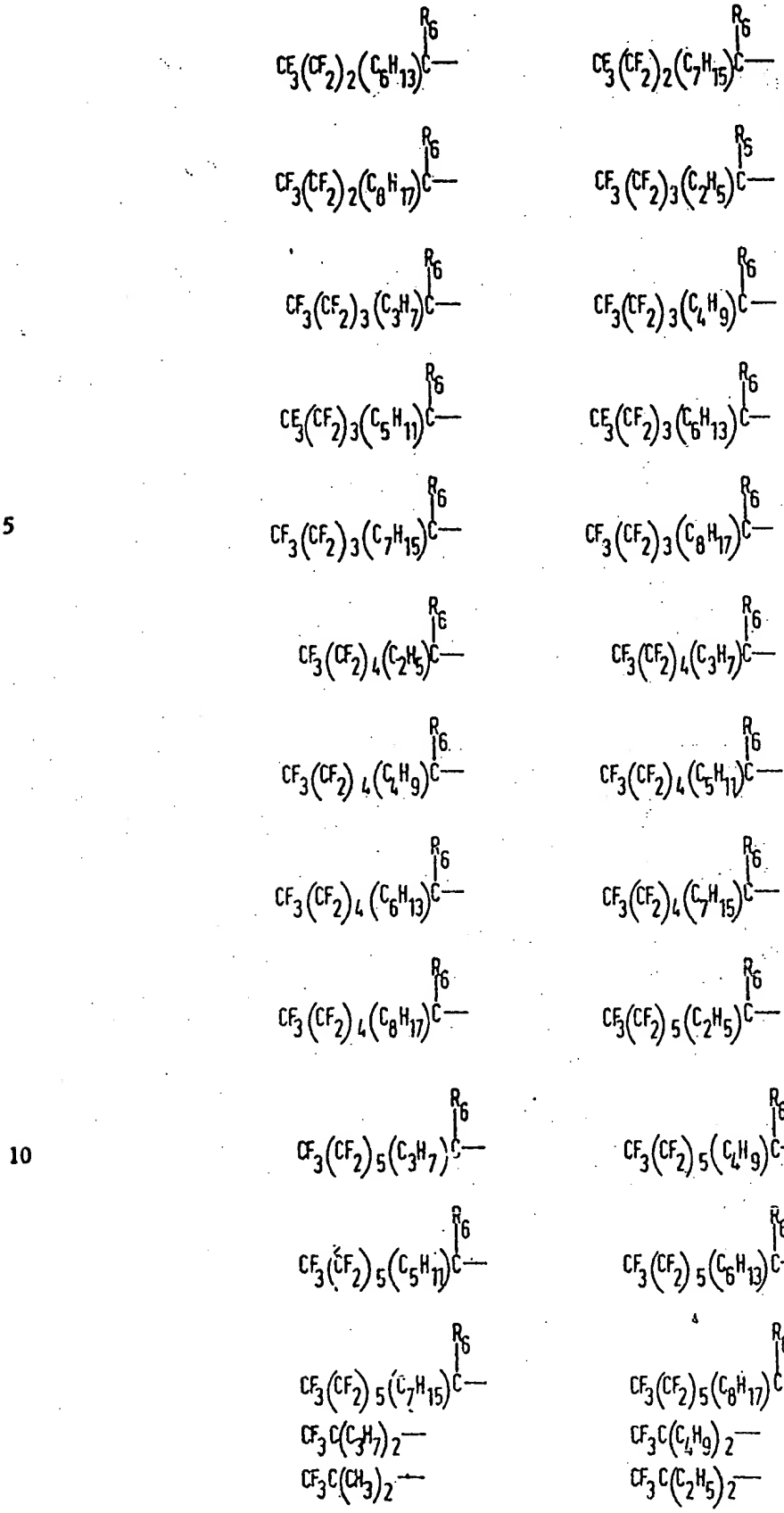
$$CF_3CF_2(C_3H_7)\overset{R_6}{\overset{|}{C}}- \qquad CF_3CF_2(C_4H_9)\overset{R_6}{\overset{|}{C}}-$$

$$CF_3CF_2(C_5H_{11})\overset{R_6}{\overset{|}{C}}- \qquad CF_3CF_2(C_6H_{13})\overset{R_6}{\overset{|}{C}}-$$

$$CF_3(C_7H_{15})\overset{R_6}{\overset{|}{C}}- \qquad CF_3CF_2(C_8H_{17})\overset{R_6}{\overset{|}{C}}-$$

$$CF_3(CF_2)_2(C_2H_5)\overset{R_6}{\overset{|}{C}}- \qquad CF_3(CF_2)_2(C_3H_7)\overset{R_6}{\overset{|}{C}}-$$

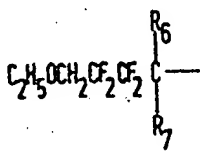
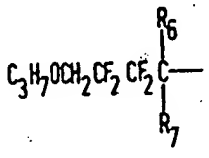
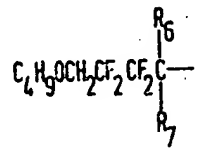
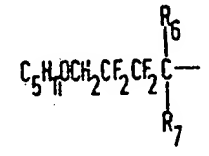
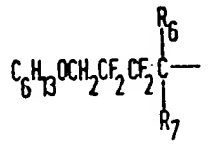
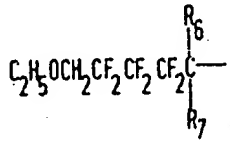
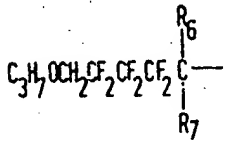
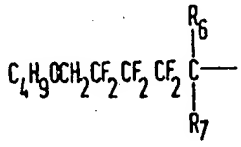
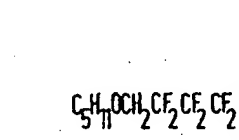
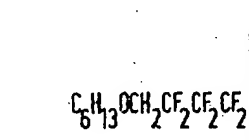
$$CF_3(CF_2)_2(C_4H_9)\overset{R_6}{\overset{|}{C}}- \qquad CF_3(CF_2)_2(C_5H_{11})\overset{R_6}{\overset{|}{C}}-$$

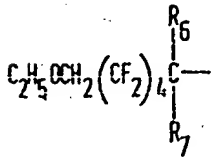
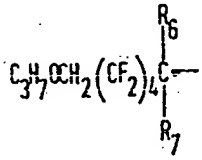
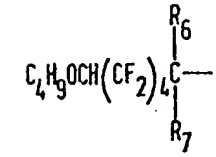
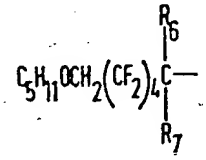
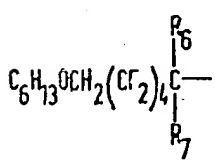


where R_6 and R_7 have their aforedescribed significance.

The halogenated alkyl radicals can be primary, secondary or tertiary.

Other suitable fluorine-containing radicals include fluorinated alkoxyalkyl radicals particularly those represented by the following formulae:

where R_6 and R_7 have their aforedescribed significance.

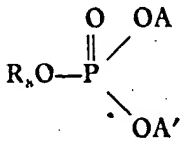
The hydrogen and the fluorine in the previously described haloalkyl radicals can be replaced by other halogens, such as chlorine or bromine.

Typical examples of aryl and substituted aryl radicals are phenyl; alkoxylated phenyl; lower alkyl substituted phenyl; phenyl cresyl and xylyl in which the available hydrogen on the phenyl or substituted phenyl is partially or totally replaced by a

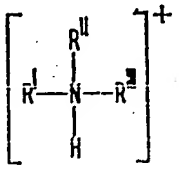
halogen, *o*-, *m*- and *p*-trifluoromethylphenyl, *o*-, *m*- and *p*-2,2,2-trifluoroethylphenyl, *o*-, *m*- and *p*-3,3,3-trifluoropropylphenyl and *o*-, *m*-, and *p*-4,4,4-trifluorobutylphenyl. Also illustrative are isopropylphenyl, butylphenyl, alpha-alkylbenzylphenyl and alpha, alpha-dialkylbenzylphenyl, e.g. alpha-methylbenzylphenyl, alpha, alpha dimethylbenzyl phenyl.

The preferred basestocks for the present invention are: the trialkyl phosphates wherein the alkyl group has from 4 to 20 carbon atoms; the triaryl phosphates wherein the aryl group is phenyl, cresyl, xylyl, isopropylphenyl and/or *alpha*-methylbenzyl, mixed alkyl aryl phosphates, i.e. aryl dialkyl phosphates and alkyl diaryl phosphates, wherein the alkyl groups have from 4 to 8 carbons and the aryl groups are phenyl, cresyl, xylyl, isopropylphenyl and alpha-methylbenzyl phenyl. The particularly preferred phosphates for the present invention are: tributyl phosphate; trihexyl phosphate; tris(n-butyl) phosphate; tri(2-ethylhexyl) phosphate, tridecyl phosphate, tricresyl phosphate, trixylyl phosphate, cresyl phenyl phosphate, xylyl cresyl phosphate, xylyl phenyl phosphate, isopropyl phenyl phenyl phosphate, alpha-methylbenzyl phenyl phosphate, diisopropylphenyl phenyl phosphate, biphenyl phenyl phosphates and mixtures thereof. The mixed aryl esters named above are intended to cover the complex mixtures of these phosphates having different ratios of the particular aryl groups named. Thus, isopropylphenyl phenyl phosphate is intended to cover the reaction product of phosphorus oxychloride and a mixture of phenol and isopropylphenol in any weight ratio of the phenols. This product will be a mixture of triphenyl phosphate, triisopropyl phenyl phosphate, phenyl bis(isopropylphenyl) phosphate and isopropylphenyl diphenyl phosphate.

The fluids of the invention contain a hydrogen phosphate ester. The term hydrogen phosphate ester includes both the dialkyl hydrogen phosphates and the alkyl dihydrogen phosphates, and the amine salts thereof. These compounds correspond to the formula:



wherein R_a is a C_1 to 20 alkyl group, A is hydrogen, a C_1 to 20 alkyl group, a heterocyclic amine group or an amine cation of the formula



wherein R', R'' and R''' are the same or different and are each a C_1 to 30 alkyl or aryl group or hydrogen; and A' is A or a C_1 to 20 alkyl group. These compounds are well known in the art and are commercially available as mixtures of both the alkyl dihydrogen phosphates and the dialkyl hydrogen phosphates or salts thereof. Illustrative of these materials are the following: dodecyl hydrogen phosphate, methyl isostearyl hydrogen phosphate, tridecyl dihydrogen phosphate, p-cresyl isostearyl hydrogen phosphate, the amine salts thereof, and mixtures thereof.

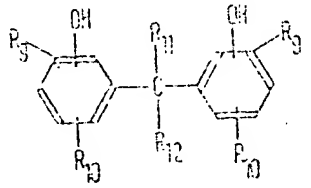
A particularly preferred alkyl hydrogen phosphate for use in the present invention is a mixed dodecyl acid phosphate sold under the trademark "ORTHOLEUM" 162 by E. I. du Pont de Nemours, Inc. of Wilmington, Delaware. This alkyl hydrogen phosphate mixture has the properties listed in Table I.

TABLE I

Specific Gravity, 60 F/60 F	0.98
Pounds per Gallon at 60 F	8.17
Color, ASTM	L 1.0
Acid Number, mg KOH/g	270
Phosphorus, wt. %	10.1
Sulfur, wt. %	0.0
Viscosity:	

Temperature, F	Sus	cs
100	380	81
210	64	11.6
Viscosity Index		130
Pour Point, F		Below 0
Freezing Point, F		53
Flash Point, F Cleveland Open Cup		320
Fire Point, F Cleveland Open Cup		360
Decomposition Temperature F		355

The other essential ingredient in the antioxidant of the present invention is a hindered phenol. The term hindered phenol as used herein means those substituted phenols having at least one alkyl group of from 3 to 8 carbon atoms attached to the phenyl ring in a position adjacent to the hydroxyl group. While any of the well known hindered phenolic antioxidants can be used in the present invention, it has been found to be particularly advantageous to use an alkylene-linked hindered bisphenol. The term alkylene-linked hindered bisphenol is meant to designate those compounds having the formula corresponding to:



wherein R, R_{10} are the same or different and are branch-chained alkyl groups having from 3 to 8 carbon atoms; R_{11} and R_{12} are the same or different and are hydrogen or C_1 to 8 alkyl; and each of the hydroxyl groups are located adjacent to at least one of the branch-chained alkyl groups. As stated above these compounds are well known in the art. Of the preferred alkylene-linked hindered bisphenols for the present invention those wherein R_{11} and R_{12} are hydrogen, i.e. the methylene-linked hindered bisphenols, have been found to be most useful and those in which R_9 and R_{10} are C_3 to 5 alkyl groups are particularly preferred. The compounds can be illustrated by the following:

4,4'-methylene bis(2,6 di-t-butyl phenol);
4,4'-methylene bis(2,6 di-t-amyl phenol);
4,4'-methylene bis(2,6 di-isopropyl phenol);
2,2'-methylene bis(3-t-butyl-6-isopropyl phenol);
4,4'-methylene bis(3-t-butyl-6-isopropyl phenol);
2,2'-methylene bis(3,4-di-t-butyl phenol);

and mixtures thereof.

The antioxidant combination of the present invention is present in an amount sufficient to stabilize the base stock against oxidative degradation. For most uses, the amount of hindered phenol will be from 0.1 to 11% by weight of the basestock and preferably from 0.5 to 2.0%. The hydrogen phosphate ester or amine salt is present in amounts from 0.005 to 3% by weight of the basestock, and preferably from 0.01 to 0.1%. It is understood that for purposes of transportation and storage, a concentrate of basestock and the antioxidant combination can be formulated such that the concentrate can be diluted with more basestock prior to use in order to bring the concentration of the antioxidant combination within the desired ranges. For example, a concentrate of basestock containing 10% by weight of alkylene-linked hindered bisphenol and 0.5% hydrogen phosphate ester or amine salt can be prepared and later diluted with 9 parts of base stock per part of concentrate to bring the antioxidant concentration down to 1% and 0.05% respectively.

The fluids of the present invention can additionally contain any of the well known additives such as: ashless dispersants of the alkoxylated alkyl phenol type; metal deactivators, such as benzotriazole and N,N' disalicylidene-1,2-dipropane diamine; and anti-foaming agents, such as the methyl silicones. Furthermore, the fluids of the present invention normally contain a viscosity index (VI) improver in an amount up to about 10% by weight. Any conventional VI improver which is compatible with the base stock of the present invention can be used. It has been found to be most advantageous to employ the polymers and copolymers of the C_{1-18} alkyl esters of acrylic and methacrylic acid having a molecular weight of from 5,000 to 50,000 as VI improvers in the present invention.

The fluids of the present invention can be used in a wide variety of applications

such as in compressors, hydraulic lifts, deck edge elevators, aircraft hydrauiic systems, brake systems, basic oxygen furnaces, die casting equipment, levelling devices, servo control units, and mining equipment, and as steam turbine lubricants.

The invention will be further illustrated by the following non-limiting examples.

EXAMPLE I

A xylyl cresyl phosphate base stock wherein the xylyl and cresyl groups are present in an approximately 4:1 weight ratio, having a viscosity of approximately 220 Saybolt Universal seconds at 100°F, is blended with 1.0% by weight of 4,4'-methylene bis-(2,6-di-t-butylphenol) to yield Fluid A. A second portion of the same base stock is blended as above and further contains 0.05% by weight of a commercially available mixture of dodecyl hydrogen phosphates sold under the trademark "ORTHOLEUM" 162 by I. E. du Point de Nemours to yield Fluid B. The two fluids described above, along with the phosphate base stock alone are tested according to modified oxidation stability tests, Fed. Test Method Std. No. 791a, Method 5308.4 and corrosion tests, ASTM D665—60. The results of these tests are contained in Table II.

TABLE II

	Basestock	Fluid A	Fluid B
Viscosity at 100°F. SUS	226	237	240
Acid Number, MgKOH/g	0.11	0.14	0.31
Oxidation Stability			
72 Hour. 347°F., Airflow=5 1/hr			
Viscosity after test, SUS	400	302	270
Percent Increase in Viscosity	77	27	13
Acid Number After Test	9.8	4.0	2.8
Attack on Metals specimens, g loss			
Mg	−0.054	−0.023	−0.054
Steel	−0.016	−0.016	−0.062
Al	−0.085	−0.100	−0.069
Ag	−0.185	−0.138	−0.123
Cu	−0.762	−0.569	+0.400
Hydrolytic Stability			
200°F. 48 Hour			
Acid content of Water Layer-mgKOH	2.7	3.3	10.4
Copper Loss, mg/cm²	0.069	0.008	0.15
Copper Appearance	Pass	Pass	Pass

The results contained in Table II clearly demonstrate the superior oxidative stability of the present invention. The increase in oxidative stability of Fluid B over Fluid A is clearly unexpected since hydrogen phosphates have not heretofore been recognized as antioxidants in any fluids, much less the phosphate fluids of the present invention. These results are also unexpected since phosphate fluids containing similar levels of hydrogen phosphates alone do not exhibit any substantial increase in oxidative stability.

EXAMPLE II

Fluid C is formulated in the same manner as Fluid B except that 0.01% by weight of ORTHOLEUM is employed. This fluid is tested in duplicate in the same manner as Example I and the results are listed in Table III.

TABLE III

	Fluid C	
	Run No. 1	Run No. 2
Percent change in viscosity Test	18.2	19.5
Acid No. Before Test (MgKOH/g)	0.06	0.06
Acid No. After Test (MgKOH/g)	3.25	2.77
Metal Weight changes, mg/cm²		
Mg	−0.038	−0.054
Steel	−0.023	−0.046
Al	−0.031	−0.023
Ag	−0.100	−0.085
Cu	−0.177	−0.315

As is evident from Table III, even when the amount of hydrogen phosphate is

reduced to one fifth of that used in Fluid B, substantial increases in oxidative stability are achieved.

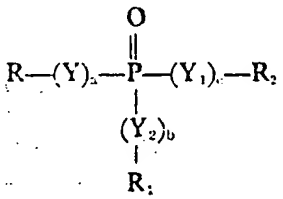
EXAMPLE III

A cresyl xylyl phenyl phosphate having the cresyl, xylyl and phenyl groups in approximately a 4:1:1 weight ratio, having a viscosity of 150 SUS at 100°F., is blended with 1.0% by weight of 4,4-methylene bis(2-6-di-t-butyl phenyl) and 0.05% by weight of "ORTHOLEUM" 162. This fluid possesses significantly higher oxidative stability than the base stock along and passes the rust test, ASTM D895, in both distilled and synthetic sea water.

WHAT WE CLAIM IS:—

1. A fluid comprising:

(a) a phosphate base stock having the formula:



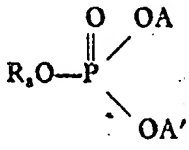
wherein Y is oxygen, sulfur or

Y_1 is oxygen sulfur or

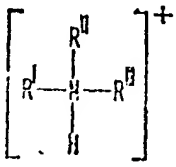
Y_2 is oxygen, sulfur or

R, R_1, R_2, R_3, R_4, and R_5 are each an alkyl, aryl, substituted aryl or substituted alkyl; and a, b and c are each 0 or 1 and the sum a+b+c is from 1 to 3; and

(b) an oxidative stabilising amount of an anti-oxidant combination of a hydrogen phosphate ester or amine salt thereof, and a hindered phenol (as herein defined), the said hydrogen phosphate ester or amine salt thereof having the formula:



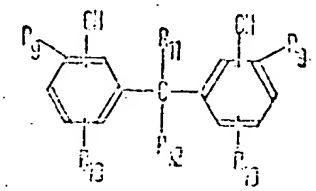
wherein R_6 is a C_{1-20} alkyl group; A is hydrogen, C_{1-20} alkyl, a heterocyclic amine group or an amine cation of the formula:



wherein R', R'' and R''' are each hydrogen or alkyl; and A' is A or a C_{1-20} alkyl group.

2. A fluid according to claim 1 which contains from 0.005 to 3.0%, by weight of the entire fluid, of said hydrogen phosphate ester or amine salt thereof, and from 0.1 to 11%, by weight of the entire fluid, of said hindered phenol.

3. A fluid according to claim 1 or 2 wherein the hindered phenol is an alkylene linked hindered bisphenol having the formula:



wherein R_9 and R_{10} are each branched chain alkyl groups having from 3 to 5 carbon atoms and R_{11} and R_{12} are each hydrogen or C_1 to C_8 alkyl, and each of the hydroxyl groups are located adjacent to at least one of the branched chain alkyl groups.

4. A fluid according to claim 3 wherein R_{11} and R_{12} are both hydrogen.

5. A fluid according to claim 3 wherein said alkylene linked hindered bisphenol is 4,4'-methylene bis(2,6-di-t-butylphenol).

6. A fluid according to claim 2, 3, 4 or 5 wherein the hydrogen phosphate ester is a mixture of dodecyl hydrogen phosphates.

7. A fluid according to claim 2, 3, 4 or 5 wherein R, R_1 and R_2 are each a phenyl, cresyl, xylyl, isopropylphenyl, biphenylyl or α-methylbenzylphenyl group.

8. A fluid according to claim 1 substantially as herein described in any of the Examples.

9. A fluid according to claim 1 wherein the phosphate base stock and/or the hydrogen phosphate ester and/or the hindered phenol is specifically hereinbefore named.

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